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Chapter 17

Application of High Performance Photoinitiating Systems for Holographic Grating Recording

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Additional information is available at the end of the chapter

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Abstract

In this chapter, a compilation of different systems able to photogenerate active radicals toward polymerization reaction(type I, type II and three component photoinitiating systems) for application in holographic grating recording when associated to monomers is reviewed. In particular, the visible curable system is associated to fluorinated acrylate monomers formulation for creation of transmission gratings. The PIS efficiencies are presented in term of diffraction grating yields and compared to photopolymerization experiments. The special case of photocyclic initiating systems is described in details, its influence on the grating built up being discussed on the basis of selected mixtures using visible dyes, electron donors (e.g. amines), electron acceptors (e.g. iodonium salts) or hydrogen donors as coinitiators. The role of the photochemical properties of dye on the performance of the holographic recording material is investigated through time resolved and steady state spectroscopic studies of the PIS (e.g. nanosecond laser flash photolysis), to highlight the photochemistry underlying active radicals photogeneration. In order to get more insight into the hologram formation, grating formation curves were compared to those of monomer to polymer conversion obtained by real time Fourier transform infrared spectroscopy (RTFTIR). This work outlines the importance of the coupling between the photoinitiating system (i.e. the photochemical reactions) and the holographic resin.

Keywords: free radical photopolymerization, photoinitiating systems, holographic recording, polymer material, diffraction gratings

1. Introduction

Photopolymerization is a chemical reaction where organic molecules exposed to UV or visible photons react to form macromolecules corresponding to high molecular weight molecules, i.e.,

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the polymer. Photopolymerizable resins usually contain a photoinitiating system (PIS) which converts light into chemical energy, a mixture of monomers, oligomers and additives [1]. The most versatile process is the free radical photopolymerization (FRPP) which offers the most important choice of materials and potential PIS. The efficiency of the PIS is determined by the light absorption properties of the photosenzitizer (PS, the molecules that absorb photons, like organic dyes), given by Beer-Lambert's law, the quantum yield of initiating radicals and the reactivity of these radicals towards the monomer. It is recognized that the photoinitiating systems is the corner stone of photopolymerization process. One application of photopolymerization is holographic recording [2, 3], for example, for information storage [4–7]. Holography also represents an interesting and growing field due to an increasing demand in security. The development of such applications is directly governed by the characteristics of the material available for holographic recording. Photopolymerizable media are promising candidates. In that case, the performance of the material is related to the photosensitivity of the photopolymer and the diffraction efficiency which could be obtained. Therefore, the design of systems for highest performances is still an interesting challenge. For instance, Acrylic monomers, which are currently used in these recording systems, have opened up in this field interesting possibilities, due to their attractive features (the complete absence of wet processing, high flexibility of the formulation, high diffraction efficiencies) [8, 9].

2. Basics of photoinitiating systems

Historically, two classes of photoinitiating systems were defined depending on the mechanisms of light conversion into chemical potential (i.e., radicals). In the first class, the photoinitiating system contains one molecule (the photoinitiator PI) which is promoted into a dissociative excited state after light absorption and undergoes a homolytic (or heterolytic) cleavage through a Norrish I photoreaction [10–12]. These type I photoinitiators produce two radicals that could be both reactive toward free radical photopolymerization (FRPP) (**Figure 1a**).

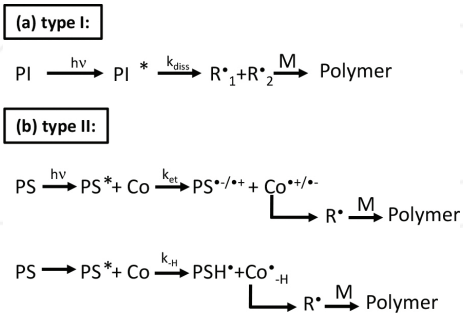
(a) type I:
PI hν PI * k_{diss} $R^{\bullet}_1$+$R^{\bullet}_2$ M Polymer
(b) type II:
PS hν PS*+ Co k_{et} $PS^{\bullet-/\bullet+}$ + $Co^{\bullet+/\bullet-}$
$R^{\bullet}$ M Polymer
PS PS*+ Co k_{-H} $PSH^{\bullet}$+$Co^{\bullet}_{-H}$
$R^{\bullet}$ M Polymer

Figure 1. Type I and type II photoinitiating systems (PIS), PI: photoinitiator, PS: photosensitizer, Co: coinitiator, $R^{\bullet}$: initiating radical, M: monomer, k_{diss}: rate constant of dissociation, k_{et}: electron transfer rate constant, k_{-H}: hydrogen abstraction rate constant.

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Among type I photoinitiators, one can find hydroxylalkylphenones, benzylketals, benzoin ether derivatives, α-aminoketones and acylphosphine oxides (**Figure 2**). In these compounds, the cleavage rate constants are high, leading to very good quantum yields of radical generation Φ_R. The quantum yield of radical generation is defined as the number of radicals formed divided by the number of absorbed photons. Some type I photoinitiating systems exhibit quantum yield as high as 0.8–1.0 [13, 14]. However, the vast majority of type I photoinitiators is only reactive under UV light [14, 15]. Only a limited set of available type I photoinitiating systems absorbs in the blue or green region. For instance, a bisbenzoylphosphine oxide derivative (Irgacure 819) exhibits an absorption spectrum extending up to around 410–420 nm. The great advantage of this class of acylphosphine is the efficient photobleaching ability that increases the photoinitiation efficiency. This is especially useful when high thickness of photopolymer is needed. However, oxygen inhibition impacts the efficiency of this class of acylphosphine oxide, which limits their applications [10]. A titanocene derivative (CG-784) absorbing in the green region was applied to the photopolymerization of some high-index organic monomers and incorporated into acrylate oligomer-based formulations, which enables irradiation at 546-nm light source [16]. Unfortunately, it seems that this compound does not produce enough initiating radicals to achieve the appropriate monomer conversion [17]. Recently, a visible light photoinitiator based on acylgermanium structure was developed, exhibiting high reactivity under 550-nm irradiation. However, its main drawback relies on the availability of the molecule (proprietary structure and synthesis) [18].

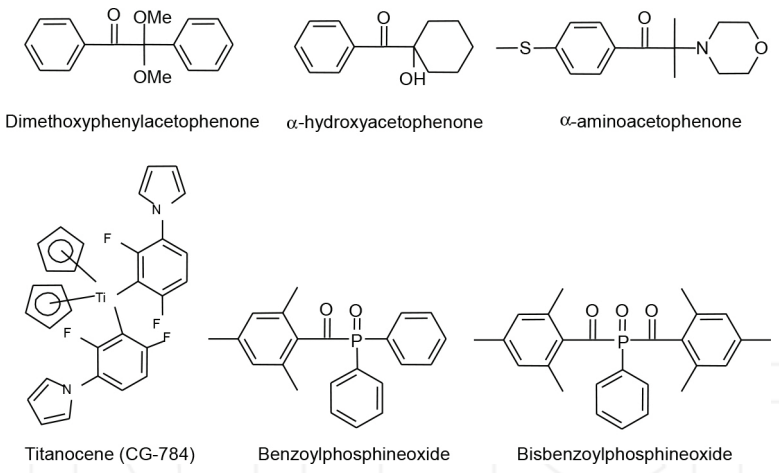

Figure 2. Examples of commercially available type I photoinitiators.

Even if type I photoinitiators can exhibit high quantum yields of radicals, their main drawback is their limited spectral sensitivity to the UV—blue region of the electromagnetic spectrum. By contrast, type II PIS are versatile initiators for UV curing systems and visible light photopolymerization. Indeed, the combination of organic dyes and coinitiators provides tremendous flexibility in the selection of irradiation wavelength from the UV to the near infra-red region.

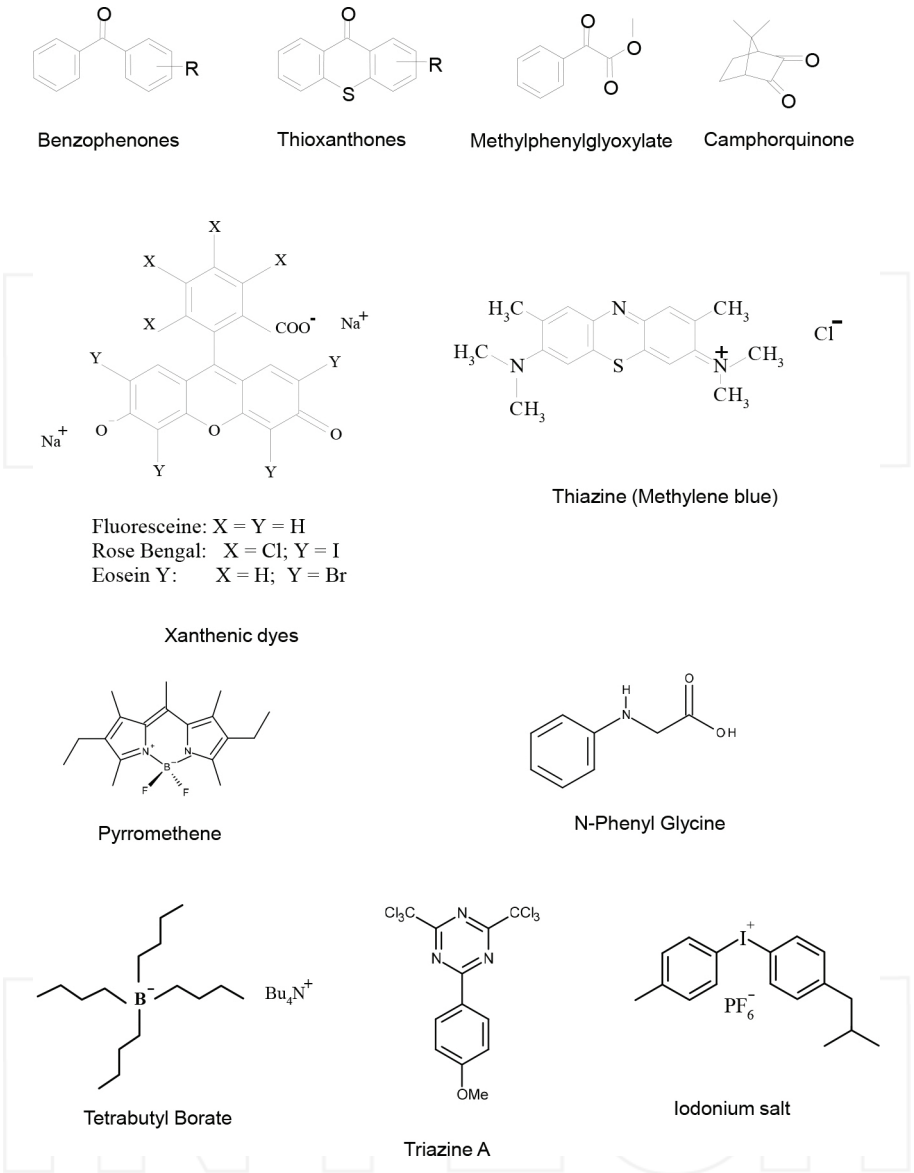

Figure 3. Examples of commercially available type II photosensitizers (PS) and coinitiators (Co).

Thus, on the contrary to type I PIs which are monomolecular, type II photoinitiating systems rely on the combination of two molecules (see **Figure 1b**). The first molecule absorbs the photon. It is the chromophore and is often called the photoinitiator (PI) or the photosensitizer (PS). The second one could be an electron donor, an electron acceptor or a hydrogen donor

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(see **Figure 1b**), the so-called coinitiator (Co), which gives the initiating radicals R• through photoreaction [19, 20]. After light absorption, the photosensitizer (PS) is promoted into one of its electronic excited states (singlet and/or triplet) from which the photochemical reaction occurs with the coinitiator (Co). One important feature of type II PIS is that the photosensitizer (PS) and the coinitiator (Co) must be selected to prevent any dark thermal reaction. Thus, photopolymerization occurs only in irradiated zones allowing a full control of the polymerization in time and space. In typical type II PIS, photosensitizers with good absorption features in the UV-blue region can be selected among benzophenones [21–28], thioxanthones [29–34], camphorquinone [35–37], benzyls [22, 38] and ketocoumarin derivatives [39–41]. For visible light PIS, the PS can be selected in whole panel of organic dyes such as, coumarins [41], xanthenic dyes [42–44], cyanine dyes [45], thiazine dyes [42], phenazine dyes and pyrromethene dyes [46–48]. The hydrogen donor coinitiators are generally amines [36, 49–54], ethers [55–57], sulfides [57–61] and thiols [61–63](see **Figure 3**). However, the ketyl radical formed on the PS moiety is generally unreactive with respect to the double bonds and could even act as a terminating agent towards the growing chain [17, 49, 64, 65]. Coinitiators reacting through electron transfer are borate salts [66, 67], iodonium salts [68–70] or triazine derivatives [47] which lead to the production of radical after a photodissociative electron transfer reaction with excited PS. However, these two components systems have limited efficiency compared to type I systems.

3. Photocyclic initiating systems

One of the reasons that could be responsible for the lower sensitivity of type II photoinitiating systems (PIS) compared to type I is their inherent chemical mechanisms. In type I PIS, the molecules are cleaved after light absorption: this is an intramolecular fast reaction. On the other side, for type II PIS, the reactions are bimolecular and can be limited by diffusion process of the photosensitizer (PS) and coinitiator (Co) (see **Figure 4**). The actual reaction rate constants of electron transfer (or H-abstraction) in such conditions can be evaluated from a simple encounter complex kinetic model (see [45] and ref. herein for more details) and is generally lowered when the viscosity of the resin increases. As a result, the efficiency of reaction is greatly impacted and the PIS becomes inefficient with low radical quantum yields.

One way to overcome the lack of reactivity of conventional type II photoinitiating systems (PIS) is to develop one molecule type II PIS where the PS and the coinitiator (Co) are chemically linked together (see **Figure 4b**). In this case, reaction rates are independent of the diffusion process and highly sensitive systems can be obtained [71–74]. However, such kind of single molecule type II photoinitiating systems (PIS) suffer of proprietary structure and synthesis costs which makes them tricky to use.

In order to enhance type II sensitivity, many groups have developed more complex photoinitiating systems by adding a third component into the PIS formulation leading to the so-called three-component photoinitiating system. Indeed, the photopolymerization efficiency of type II PIS can be greatly improved by introducing an additive, which yields to an additional radical

formation through reaction with one photoproduct arising from the photochemical reaction [75–78]. The use of photoinitiating systems based on three components keeps the tremendous flexibility of the light sources and the determination of the actinic wavelength, because the wide variety of dyes that may be used in type II PIS is still large. Three different kinds of additives can be used: (1) latent species that create reactive centers after reaction, (2) molecules that are oxidized and (3) molecules that are reduced [47, 48, 79, 80]. The first class of usable additives are species that leads to the formation of reactive centers after reaction, containing chain transfer agents such as S-H, P-H, Si-H or Ge-H-based molecules. They have found only limited applications and will not be discussed further. Among oxidable molecules that can be selected, one can find amine derivatives such *N*-methyldiethanolamine [23, 24] or triethylamine [79] as common electron donor reported to date for the photoinitiating systems in the literature. To circumvent the toxicity of alkyl amines, aromatic amines such as *N*-phenylglycine are available [32]. Triarylalkyl borates, sulfur- or tin- containing compounds, sulfinates [81] have also been reported as well as, amides, ethers, ferrocene, metallocenes, ureas, salts of xanthanates, salts of tetraphenylboronic acid, etc. It should be mentioned that the oxidation potential of the donor plays a key role in the mechanism of electron transfer.

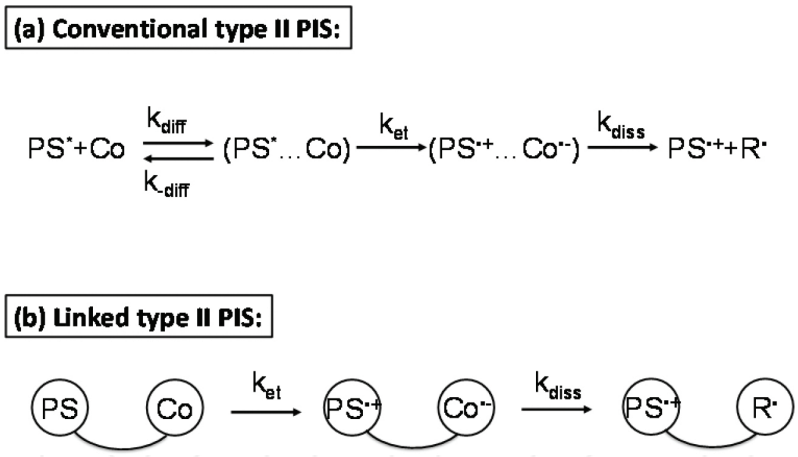

Figure 4. Reaction scheme of conventional type II photoinitiating systems (PIS) (a) and unimolecular type II PIS (b); PS: photosensitizer, Co: coinitiator, R•: initiating radical, k_{diff}: diffusion rate constant, k_{-diff}: separation rate constant, k_{diss}: rate constant of dissociation, k_{et}: electron transfer rate constant.

Electron acceptor additives (i.e., reducible additives) most commonly used are iodonium salts which exhibit a low reduction potential [14, 17, 82–85]. It is possible to introduce bromo compounds instead of the iodonium salts [24, 86]. Triazine derivatives are one of the most common electron acceptors used as third component for PIS based on dye/borate salts [87], while alcoxypyridinium derivatives were also used as a third component to increase the sensitivity of borate salts based two component PIS [88]. Other oxidative additives can be selected such as peroxides, sulfonium and pyridinium salts, iron arene complexes, and

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hexaarylbisimidazole as alternatives to iodoniums or triazines. The reduction potential of the third component is an important criterion to select the compound [46, 47].

The dyes reported in the literature as photosensitizers for type II photoinitiating systems can be used for three-component photoinitiating systems (PIS): coumarin dyes, xanthene dyes, acridine dyes, thiazoles dyes, thiazine dyes, oxazine dyes, azine dyes, aminoketone dyes, porphyrins, aromatic polycyclic hydrocarbons, aminothiaryl methanes, merocyanines dyes, squarylium dyes, pyridinium dyes, etc. Many studies reported that the photopolymerization efficiency, kinetics and mechanistic reactivity of this type of systems [41, 46–49, 64, 75–79, 86, 88–93]. However, for type II and three-components PIS, the selection of dye must respect some key criteria:

i. High absorption coefficient (ε) at the irradiation wavelength (Beer-Lambert's law);

ii. According to the bimolecular nature of type II and three-components PIS, the excited state lifetime must be as high as possible. For this reason, triplet state PS should be preferred. Singlet excited states could be used but, as singlet state lifetime are around ns, their efficiency will be lower compared to μs lifetime triplet state PS;

iii. Excited state photophysic: according to (ii), high triplet state quantum yields PS should be favored;

iv. The oxido-reduction properties of the dye (and coinitiators) are of prime importance (see **Figure 5**). Indeed, according to Rhem and Weller [94], the photoinduced electron transfer (PET) rate is related to the Gibbs free energy variation ΔG_{ET} accompanying the reaction, $\Delta G_{ET} = F(E_{ox} - E_{red}) - E^* + CT$, which after conversion in eV by diving by Avogadro number and by the charge of an electron can be expressed as follow: $\Delta G_{ET} = (E_{ox} - E_{red}) - E^* + CT$, where E_{ox} is the oxidation potential of the donor (expressed in V), E_{red} the reduction potential of the acceptor (in V), E^* (expressed in eV) the excited (triplet or singlet) state energy of the dye and F the Faraday constant. It is assumed that the Coulombic term CT is negligible. The PET must be as much exergonic as possible. Thus, in order to favor photooxidation, the dye's E_{ox} should be as low as possible, while the E_{red} of the coinitiator must be as high as possible (it is normally a negative value). The same argument can be applied to a photoreduction of dyes. Whatsoever, it is evident that the highest the E^*, i.e., the excited state energy of the dye, the most favorable is be the PET reaction. Thus, high energy excited states should also be preferred. Finally, as no thermal electron transfer should occur, ground state ΔG_{ET} must be positive (see **Figure 5**).

A full description of the electron transfer reactions occurring in three-components (and type II) PIS is summarized in **Figure 5**. Four electron transfer reactions are identified: the first one (**Figure 5** [1]) is the thermal electron transfer (ET) which should be avoided; the second one is the photoinduced electron transfer (PET) (**Figure 5** [2]) and is discussed in point iv. (vide supra), the third one is the so-called back electron transfer (BET) (**Figure 5** [3]), an intra-encounter complex recombination of reduced photosensitizer (PS) an oxidized coinitiator (Co) which gives the reactants back and lower the quantum yield of radical generation. Up to this point,

this thermodynamic approach covers also the type II photoinitiating systems requirements. Finally, if ever the fourth electron transfer reaction occurs (**Figure 5** [4]), the reduced PS is oxidized by the third component and the PS is regenerated while a second initiating radical is produced. This leads to the so-called photocyclic (or photocatalytic) initiating systems (PCIS) (vide infra). Detailed explanation of PCIS kinetics and thermodynamics can be found in Ref. [95]. However, obtaining a photocyclic behavior in three-component systems is not straighforward and great care must be taken when combining dyes and coinitiators.

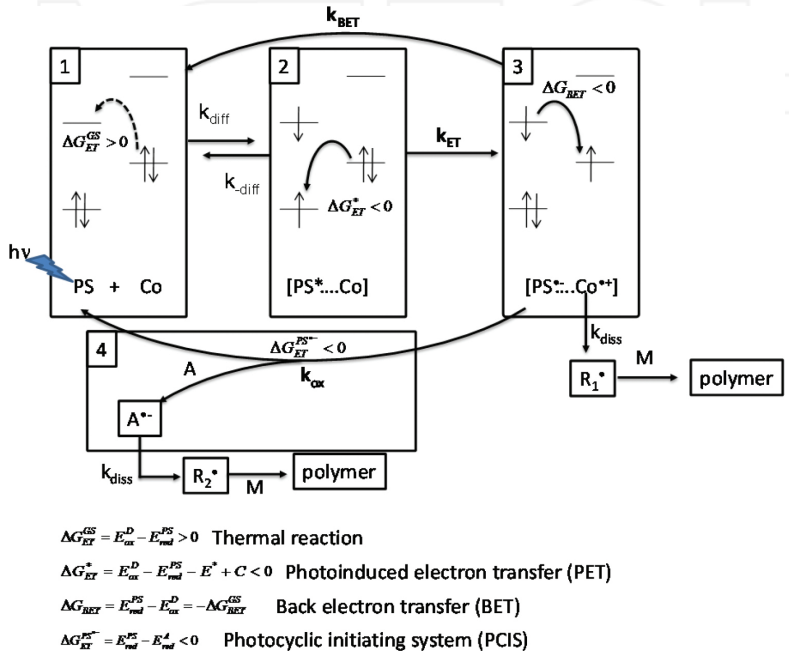

Figure 5. Thermodynamics of an oxidative three-components PCIS [1], ground state reaction ($\Delta G_{\mathrm{ET}}^{\mathrm{GS}}$) [2], excited state reaction ($\Delta G_{\mathrm{ET}}^{*}$) [3], back electron transfer (BET, ΔG_{BET}) [4], PS regeneration ($\Delta G_{\mathrm{ET}}^{\mathrm{PS}^{\bullet+}}$) in photocyclic initiating system (PCIS vide infra).

Thus, in the case of three-components PIS, two mechanisms have been observed leading to two general classes (see **Figure 6**):

a. Parallel reactions in which the coinitiators Co and the additive A react with the excited state of the dye independently (**Figure 6a**);

b. (b) Sequential reactions in which, for example, the Co reacts first through PET with the dye excited state (**Figure 6b**) leading to reduced PS and a first initiating radical. Then, the reduced PS can react with the additive A to regenerate the PS and give a second initiating radical.

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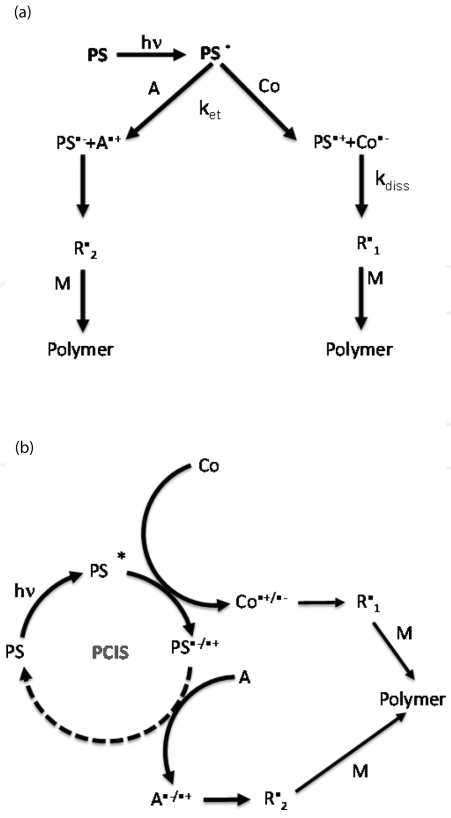

Figure 6. General reaction mechanism occurring in three-component photoinitiating systems, (a) parallel mechanisms, (b) photocyclic initiating system (PCIS).

In parallel (i.e., independent and competitive) reactions, the total yield of radicals depends on the reactivity of each coinitiator with the excited state and is not very interesting. The sequential reactions present more attractive features. This mechanism yields two advantages: the additive (A) leads to the formation of supplementary initiating radical, and the ground state dye is recovered and can be involved in further photoreactions. Therefore, a real cyclic photoreaction occurs until complete depletion of reactants. Moreover, the maximum theoretical quantum yields of PCIS are two, meaning that one absorbed photon can give two initiating radicals.

4. Photoinitiating systems for holographic recording

Holographic polymerization recording is a very particular application of photopolymerization: a three-dimensional image is built through inhomogeneous polymerization when the interference pattern illuminates the photosentive medium [5–7]. Indeed, photopolymerization

is ideally suited for such application as the reaction can be spatially and temporally controlled. Holographic elements, reversible holograms and switchable holographic gratings have been created by this method [5, 96–99]. Since the 1970s, photopolymers were developed in holography as media able to record an interference pattern or small series of pattern, through building-up of refractive index variations or relief profiles [100–102]. During volume hologram recording in a photopolymer, a complex fringe pattern with small features at the micrometer scale is recorded. The local incident variations of irradiance induce inhomogeneous photopolymerization of the photosensitive recording medium at the sub-micrometer scale leading to refractive index modulations in the hologram. Many physical and chemical processes are involved in the holographic recording: photochemical conversion of the sensitizer, of the monomer, mass transport (being a consequence of the formation of spatial concentration gradients of monomer and sensitizer), hardening of the polymer matrix, etc. Therefore, formulating the material requires a fair knowledge of all these processes, which is not a straightforward way as many parameters must be taken into account [4, 103, 104].

Many PIS can be used for holographic recording applications. Titanocene derivative Bis(η5-2,4-cylcopentadien-1-yl)-bis (2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium, Irgacure®784, was used for the optimization of several high index organic monomers into high optical quality acrylate oligomer-based formulation and compared to the type II PIS [105]. However, even if it is a one molecule process by-products that can alter recoding are formed [106]. Moreover, by introducing with these type I titanocene compounds, nanoparticles in the holographic polymer, the effect of nanoparticles concentration and size, as well as the benefic effect of chain transfer agent were studied [107, 108]. Triphenylphosphine (TPO) type I PIS was used for initiating thiol-ene photopolymerization in a composite holographic resin containing nanoparticles in a way to reduce shrinkage and enhance Δn_{sat} [109]. Near UV type I photoinitiator Irgacure 1700 was used to study the effect of surface modified ZrO_2 and TiO_2 nanoparticles, allowing high refractive index modulation and better stability against UV light [110].

A widely used type II PIS is the combination of phenanthrenequinone (PQ) with methacrylates (MA) monomers and oligomers (PMMA) [111–116]: in this case, the PQ is supposed to directly react with PMMA in its triplet state by hydrogen abstraction [112, 113]. Among other Type II PIS, methylene blue (MB) and rose Bengal (RB) have been tested in crylamide and polyvinylalcohol films [42] under 633 or 514 nm irradiation, diffraction efficiencies of 65 and 35%, and sensitivities of 30 and 100 mJ cm^{-2} have been, respectively, reached, with a spatial resolution of *ca.* 1000 lines mm^{-1}.

The influence of photonic and chemical parameters on the holographic recording capabilities and photochemical bleaching process of a series of xanthene dyes such as RB, eosin Y (EY), erythrosin B (ErB), fluorescein (F) and rhodamine B (RoB) has been investigated with triethanolamine (TEA) as electron donor Co [117, 118]. The photobleaching efficiency, i.e., the ability of the PS to lose their tint, followed the order ErB > EY > RB > RoB > F. The highest photobleaching rate constant of ErB PIS was invoqued to explain the higher diffraction efficiency obtained compared to EY, RB, RoB and F under the same experimental conditions. More recently, the same family of xanthenic dyes was theoretically and experimentally investigated [119].

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A system using EY, F, MB and thionine (TH) as photosensitizers with morpholine, dimethylaminoethanol and piperidine as electron donors, and an oligourethane-acrylates resin has been used for holographic applications such as interferometry and pattern recognition systems [120]. A sufficiently high speed of recording in the 460–540 nm range has been noticed. Despite higher absorbance in the longer wavelength, holographic experiment in the red light with the MB systems outlined low reactivity and slow recording rates. More recently, combination of MB and trimethylamine (TEA) as coinitiator was still used as type II PIS in holographic recording systems bearing metallic ions as dopers to enhance holographic sensitivity efficiency [121, 122].

If type II photoinitiating systems (PIS) are widely used in holographic recording, the use of three-components PIS is less common. The efficiency of a three-component PIS based on hexaarylbisimidazole derivative (HABI), associated to a chain transfer agent 2-mercaptobenzooxazole (MBO) and 2,5-bis[[(4-diethylamino)phenyl] methylene] cyclopentanone (DEAW) as the PS incorporated into high optical quality acrylate oligomer-based formulations was reported [105] (see **Figure 7**).

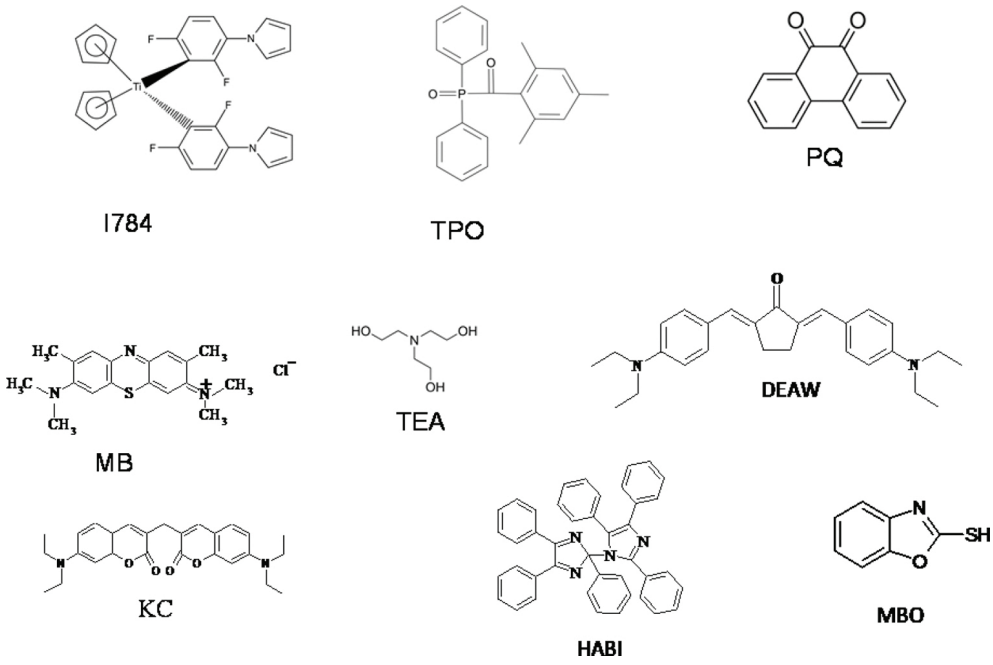

Figure 7. Structures of some PIS compounds; Bis(η5-2,4-cylcopentadien-1-yl)-bis (2,6-difluoro-3-(1H-pyrrol-1-yl)-phenyl) titanium: Irgacur®784, 2,4,6-Trimethylbenzoyl-diphenylphosphine oxide: Darocur® TPO, phenanthrenequinone: PQ, methylene blue: MB, triethanolamine: TEA; 2-mercaptobenzooxazole: MBO, 2,5-bis[[(4-diethylamino)phenyl] methylene] cyclopentanone: DEAW, hexaarylbisimidazole: HABI, 3-3′-carbonyl-bis-7-diethylaminocoumarin: KC.

Another three-component photosensitive resin, based on a 3-3′-carbonyl-bis-7-diethylaminocoumarin (KC) PS, *N*-phenylglycine (NPG) and diphenyl iodonium chloride (DPI) has been used to record holograms at 488 nm (Ar^+ laser). A diffraction efficiency around 51% corresponding to a refractive index modulation of 0.013 was obtained [123]. The efficiency of PIS based on new original synthesized dyes that could be sensitive to He-Ne laser line (632.8 nm), a HABI derivative and 3-mercapto-4-methyl-4H-1,2,4-triazole (MTA), was studied [124]. A 80% diffraction efficiency was obtained, with good physical and chemical stability under ambient conditions. The singlet excited state reactivity of bipyrromethene-BF_2 complexes (also known as BODIPY) was used in amine-free photosensitive hydrophobic binder resin as an alternative to xanthene dyes-based redox PIS [125]. The unbleached final gratings showed diffraction efficiency of 85% with good sensitivity in the 457–520 nm range.

5. Influence of photoinitiating system on holographic recording

In summary, this survey of the literature shows that most of the photoinitiating systems used for holographic recording are simple classical type I or type II PIS. Three components combination in holographic resins are less common. Moreover, the exact photochemistry underlying the initiating radical generation is not very well-known, and the effect of the PIS photochemistry on hologram formation was rarely questioned [126–128]. Furthermore, it is difficult to compare and gather holographic recording resin results, many different PIS systems are available and can be associated to various polymerizable resin, with or without binders, for use in different optical setup with diverse photonic parameters.

However, in a recent work, the influence of photochemistry on the holographic recording efficiency was performed by our group in collaboration with Bayer material science team [129]. It was shown that the prediction and interpretation of the holographic performance of a photosensitive resin containing a type II photo initiating systems is directly related to the reactivity of the dyes excited states involved and to the intrinsic properties of the photopolymerizable medium. Indeed the radical quantum yield of the dyes (RB and SFH^+) coupled to borates salt electron donor coinitiator was fixed by the viscosity of the holographic resin matrix and the redox properties of the dyes and borates. A method was proposed to calculate the initial yield of initiating radicals. It was found that this radical formation quantum yield directly governs not only the maximum rate constant of photopolymerization, but also the final diffraction efficiency.

With this in mind, we have recently tailored different three-components photoinitiating systems for holographic recording with the advantage that all measurements were performed on the same holographic resin formulation, under fixed experimental conditions in a given holographic recording setup [130–132]. Furthermore, the holographic results were compared to the visible curing of the holographic resin formulation followed by real-time FTIR spectroscopy [130–134]. RT-FTIR allowed the study of free radical polymerization (FRP) by following the disappearance of C-C double bonds in monomer (see Ref. [131–133] for more detail): it permitted to measure the final monomer conversion into polymer and the rate of double bond

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consumption during the polymerization reaction R_c (s^{-1}) (see **Figure 8a**). The IR spectra were recorded during sample irradiation using a green laser diode emitting at 532 nm (Roithner Lasertechnik, 50 mW) which was adapted to the FTIR spectrometer by a light guide (see **Figure 8a**). The irradiation intensity was adjusted at 25 mW/cm² on the sample. To prevent the diffusion of oxygen into the sample during the irradiation, experiments were carried out by laminating the resin between two polypropylene films and two CaF_2 windows. The thickness of the sample was adjusted using a 25-µm Teflon spacer. The spectra were recorded between 600 and 3900 cm^{-1}. The kinetics of the polymerization were measured by following the disappearance of the C-C bond stretching signal at 1637 cm^{-1}. The degree of conversion was directly related to the decrease in peak area at 1637 cm^{-1} according to:

$$C = \frac{(A_{1637})_0 - (A_{1637})_{t0}}{(A_{1637})_0} \quad (1)$$

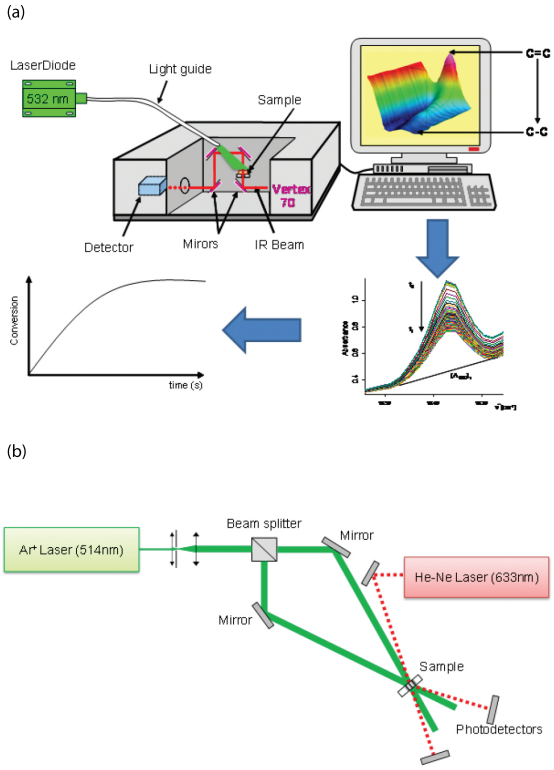

Figure 8. RT-FTIR (a) and Holographic grating recording (b) setup.

where $(A_{1637})_0$ and $(A_{1637})_t$ were the area of the IR absorption band at 1637 cm^{-1} of the sample before exposure and at time t, respectively.

Holographic gratings were recorded in transmission at 514 nm for a spatial frequency of 1000 lines mm^{-1} transmission grating in the resin with a 514 nm actinic laser. For that purpose, the samples are prepared by embedding the photopolymerizable formulation between two glass-substrates. Calibrated glass beads were used as spacers to guarantee the thickness of the system around 20 μm. The photopolymerizable system was irradiated by the sinusoidal interference pattern of two incident s-polarized beams of equal intensity, corresponding to a total power density of 25 mW/cm^2 on the photosensitive sample with a beam diameter of 2.5 cm (**Figure 8b**). Inhomogeneous polymerization reaction and dye bleaching took place leading to a modulation of the refractive index, giving rise to thick phase volume diffraction gratings. The fact that no chemical posttreatment was needed for this recording medium used, allowed the continuous follow up of the process during exposure with an inactinic reading light beam (HeNe laser at 633 nm) which was more or less diffracted (see **Figure 8b**). The diffraction efficiency at 633 nm (η) was defined by the ratio of the intensity of the first diffraction order to the diffracted plus transmitted light intensities.

The holographic resin was a mixture of different monomers and additives: the choice of the formulation was governed by earlier experiments performed in the field of visible curable systems and use of fluorinated acrylate monomers for the recording of holographic polymer-dispersed liquid crystals (LC) transmission gratings. This self-developing formulation contained:

- 45 wt% of a hexafunctional aliphatic urethane acrylate oligomer (Ebecryl 1290, Cytec) acting as primary oligomer;
- 22.5 wt% of 1,1,1,3,3,3-hexafluoroisopropyl acrylate and 22.5 wt% of vinyl neononanoate, both from Sigma-Aldrich (France). The vinyl ester monomer is known to copolymerize very easily with acrylic monomers;
- 5 wt% of *N*-vinyl-2-pyrrolidinone (Sigma-Aldrich, France) which is a standard additive introduced in photopolymerizable systems here to favor compounds solubility;
- 5 wt% of Trimethylpropane tris (3-mercaptopropionate) (Sigma-Aldrich, France) which is a trifunctional thiol able to increase the photopolymerization rate in air and leading to higher monomer conversion. These compounds were used as received. The chemical structures of the reagents used for the preparation of holographic resin can be found in Ref [132].

An example of RT-FTIR monomer conversion of the holographic resin as a function of irradiation time is given on **Figure 9b**. The photoinitiaitng system was based on Safranine O (SFH^+) as photosensitizer (PS), EDB as an electron donor and Triazine A electron acceptor (see **Figure 3** for molecular structures) as the third component. It can be seen that going from two components type II to three-components PIS increases both the rate of conversion R_c and the final conversion C_f. The same observation is valid for measured diffraction yield as a function of irradiation time (**Figure 9a**): both the formation building up time of the diffraction grating and the final diffraction efficiency increase.

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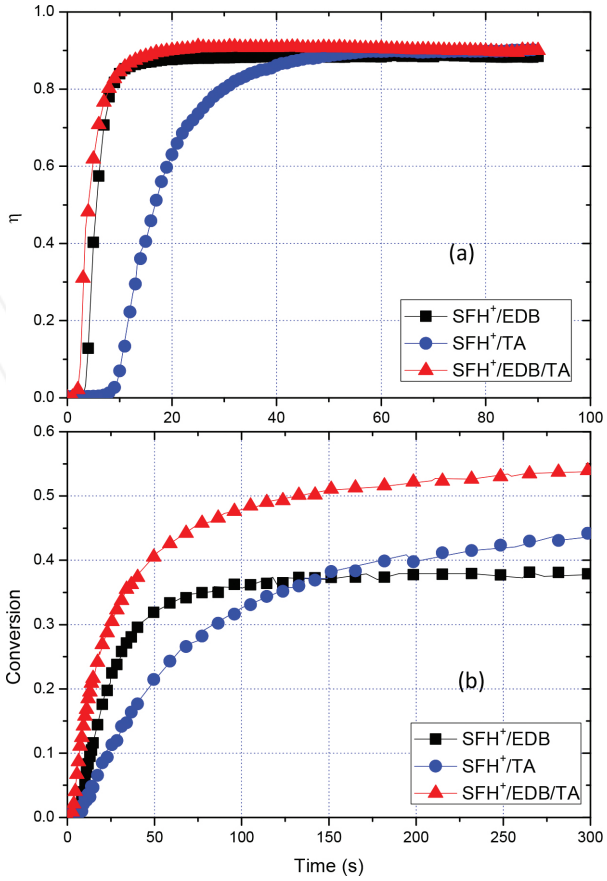

Figure 9. Evolution of the diffraction efficiency η during grating writing (a) of SFH^+ PIS and corresponding monomer conversion curves as a function of irradiation time (b).

Moreover, besides RT-FTIR and holographic measurements, a complete and detailed study of the photochemical reaction of the PIS was performed. For this purpose, steady state (UV-Vis, fluorescence) and time resolved (laser flash photolysis, time correlated single photon counting, etc.) spectroscopies were used. The first system was based on the singlet excited state reactivity of Bipyrromethene-BF_2 complexes (EMP) combined with an amine (EDB) and two electron acceptor (TA, I250) [130]. The two other systems were based on the reactivity of the triplet excited state of two dyes, RB and Safranine O (SFH^+) [131, 132]. In the first one, the reactivity of RB was compared to the reactivity of SFH^+ when combined to NPG electron donor coinitiator and HABI as additive third component [131]. In the last system, SFH^+ was combined with one electron donor (EDB) and one electron acceptor. However, it was demonstrated that no photocycle occurred in these PIS (see **Figure 9** [2, 3]). [133] Indeed, besides the nature of the excited state involved in the radical photogeneration process, it was shown that EMP PIS

exhibited a photocyclic behavior (i.e., forms a PCIS) while RB and SFH^+ PIS presented a parallel behavior (see **Figure 10**).

In order to understand correctly Scheme 2 in **Figure 10**, Hexaarylbiimidazole (HABI) derivatives deserve a little more explanations. HABI (Scheme 1 in **Figure 10**) was first synthesized by Hayashi and Maeda (see [134] and ref. Herein). It was proved that the two imidazolyl rings are twisted almost 90° relative to each other [134]. The bond energy of C-N in ClHABI is very low, which easily leads to the homolytic cleavage of ClHABI when exposed to the UV light or heated [135] to a pair of triarylimidazolyl radicals (lophyl radicals = $L^\bullet$). The lophyl radical ($L^\bullet$) is known to be a poor initiator of free radical polymerization, because of both high stability [135–137]. However, the lophyl radical is an excellent hydrogen atom abstractor, and this can be exploited in initiation using a hydrogen donor coinitiator (Scheme 2 in **Figure 10**).

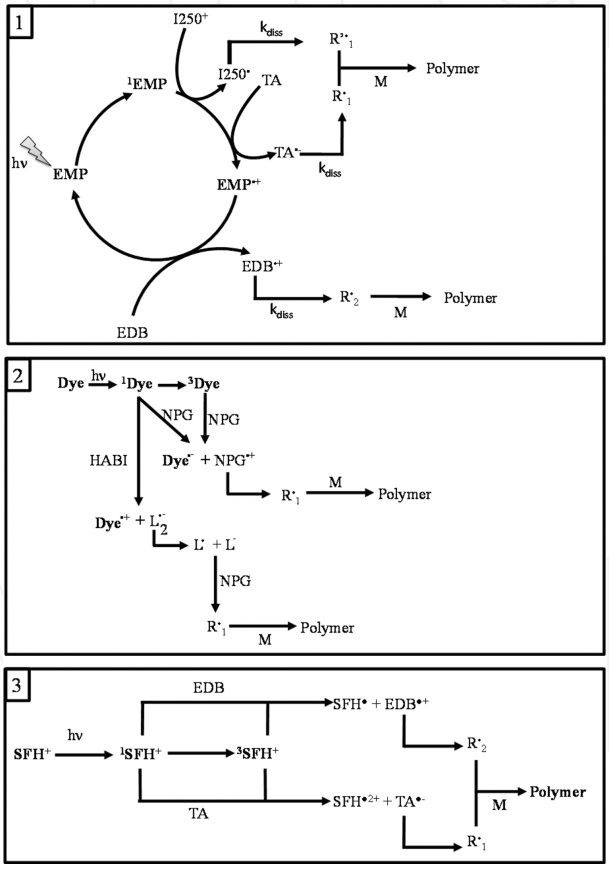

Figure 10. Photochemical mechanism underlying the radical photogeneration of [1] pyrromethene-based photocyclic initiating system (PCIS) [2], RB and SHF^+ where $L^\bullet$ stands for lophyl radical, i.e., the moiety of a HABI molecule (see text) [3], SFH^+ with one reductant and one oxidant coinitiators.

PIS	C_f	η_f	R_η(s^{-1})	R_c (s^{-1})
RB-NPG	0.52	0.78	0.25	6.0
RB-ClHABI	0.22	0	0	0.3
RB-NPG-ClHABI	0.63	0.4	0.27	8.0
SFH^+-NPG	0.3	0.95	0.41	16
SFH^+-ClHABI	0.39	0.88	0.12	1.6
SFH^+-NPG-ClHABI	0.34	0.95	0.55	20
EMP-EDB	0.44	0	0	0.8
EMP-TA	0.52	0.32	0.025	1.2
EMP-EDB-TA	0.55	0.66	0.033	1.4
EMP-I 250	0.54	0.94	0.21	2.3
EMP-EDB-I 250	0.55	0.40	0.23	2.5
EMP-NPG		0	0	0.9
EMP-NPG-I250		0.25	0.25	6.3
SFH+-EDB	0.37	0.89	0.26	1.3
SFH+-TA	0.37	0.88	0.08	0.42
SFH+-EDB-TA	0.51	0.91	0.31	2.1

Table 1. Holographic and RT-FTIR characterization of the 16 PIS combination [131–133]. η_f: final diffraction yield, C_f: final conversion in FRP, R_η: maximum rate of grating formation, R_c: maximum rate of monomer conversion.

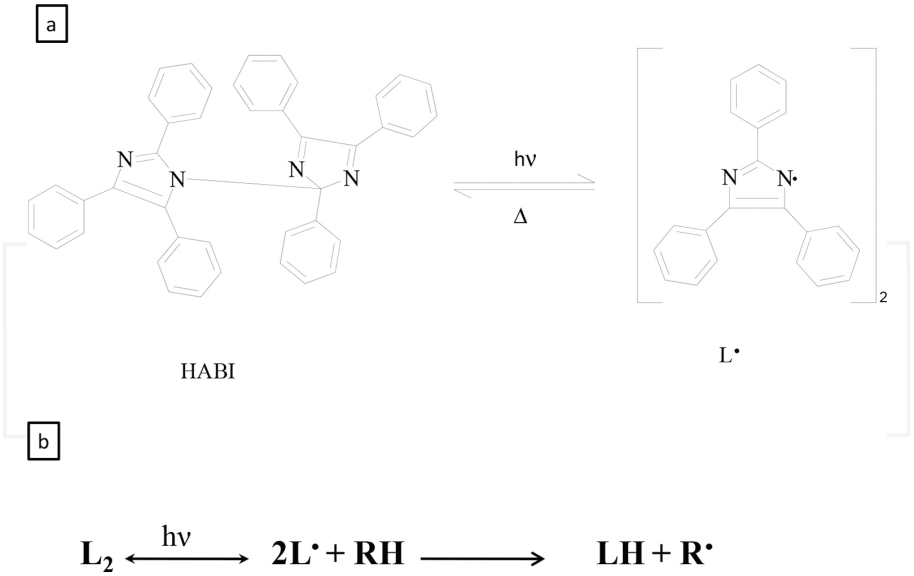

Figure 11. (a) Reversible photodissociation of HABI (L_2) into two lophyl radicals L•; (b) reaction of lophyl radical with hydrogen donor (RH).

Indeed, we have here a very unique combination of photosensitzers, coinitiators and third components showing very different mechanisms of radical photogeneration. With the three PIS presented here, 16 different combinations of PS-Co, PS-additive and PS-Co-additive were measured both in real-time FTIR (RT-FTIR) and holographic recording. The results in term of both FRP and holographic recording of these combinations are summarized in **Table 1**. The performance of the PIS toward homogeneous-free radical photopolymerization are given by the final conversion C_f and maximum rate of conversion R_c (s^{-1}), while the gratings are characterized by their final diffraction yield η_f and maximum rate of grating formation R_η (s^{-1}).

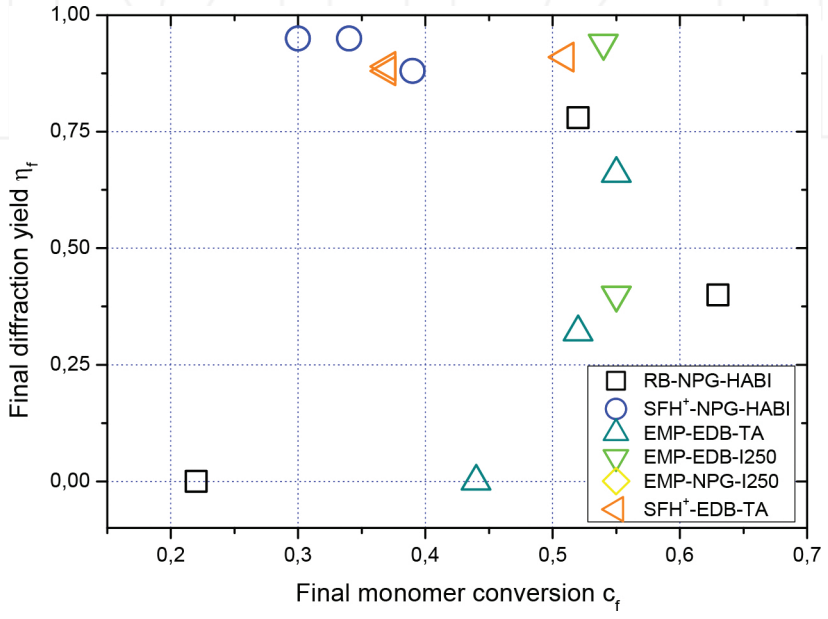

Figure 12. Final diffraction efficiency of grating recording η_f as a function of final monomer conversion C_f.

The existence of a relationship between the evolution of monomer conversion under uniform irradiation (FRP) and that of diffraction efficiency under holographic exposure is not straightforward. In **Figure 11**, the final diffraction yield η_f is plotted as a function of the final monomer conversion C_f.

Figure 12 shows that no clear correlation exists between the final conversion C_f achieved in homogeneous FRP and grating efficiency η_f.

The picture is completely different when the maximum rate of grating formation R_η are plotted as a function of the corresponding maximum rate of monomer conversion R_c. As can be seen in **Figure 13**, a monotonic curve is obtained despite the various photochemical reactions and photopolymerization kinetics of the 16 PS-Co combinations.

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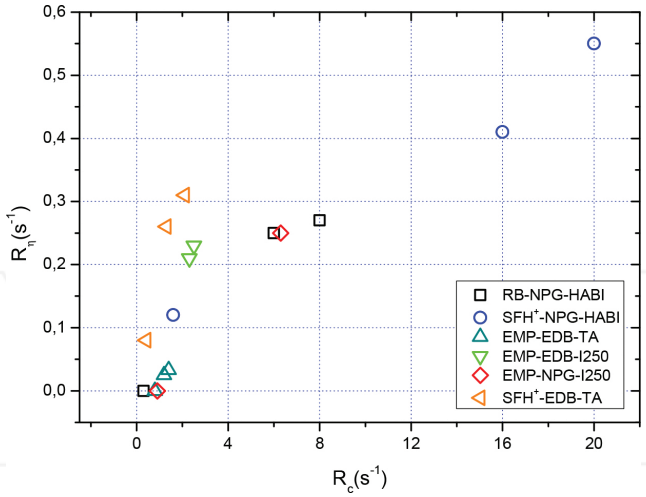

Figure 13. Maximum rate of grating formation R_η as a function of the maximum rate of conversion R_c.

The faster is the monomer conversion R_c, the faster is the building up of the diffraction grating R_η. Therefore, as the holographic resin is always the same for all these experiments, the key role in the grating formation is the number of active radicals locally created and capable of initiating the polymerization. Indeed, the fast polymerization of the monomer mixture in the bright fringes of the interference pattern results in the fast formation of refractive index modulation in the medium. On **Figure 13**, it is clearly seen that two regimes are present, each one showing a quasi linear relation between R_η and R_c with a saturation effect occurring for R_c higher than around 4 s^{-1}. At low R_c, i.e., lower than 4 s^{-1}, the mass transport of reactants (PIS, monomers, fillers, etc.) needed to build the index modulation is not limited by a too fast jellification of the medium during polymerization and high refractive index modulation can be obtained. While at higher R_c (i.e., >4 s^{-1}), the faster polymerization of the resin in the bright areas leads to a sooner freezing of the resin, preventing the mass transport effect needed for high index modulation building up, resulting in lower grating efficiency.

Thus, the coupling between PIS and holographic grating recording is not easy, and a fine tuning of the photonic parameters, holographic material, with a good comprehension of the photochemistry underlying the radical photogeneration is needed to tailor photopolymerizable systems to holographic recording, i.e., PIS-resin couple. Moreover, during our work [131–133], it appears that holographic recording reveals differences in photoinitiating system reactivity that are not detected with classical RT-FTIR measurements.

6. Conclusion

In this chapter, it was shown that many photoinitiating systems are usable for holographic polymerization. Type I and type II are widely exploited even if they are not the most efficient

in term of radical quantum yields (especially, visible type I PIS). If in the UV-vis curing and photopolymerization field, three-components systems are widely described and used, because they proved high reactivity in photopolymerization reactions, their application is not so much developed for holographic recording through polymerization. This can be due to higher complexity of the photochemistry and choice of components, as described in this chapter. However, it was shown that three-component photoinitiating systems can be great choice for application in holographic recording: high diffraction grating building rates with high final diffraction yields were obtained paving the way toward highly sensitive holographic materials. Even if photopolymerization and holographic recording is not straightforward, the challenge is worth and the need to improve both photosensitivity and diffraction efficiency of a photopolymerizable recording medium is certainly the driving force to pay more attention on the development of three-components and photocyclic initiating systems specifically designed for such application. As many different physical and chemical processes (photochemistry of the PIS, monomer, mass transport and gelation of the polymer matrix) are taking place in the medium to give rise to index modulation. Optimizing the material requires a fair knowledge of all these processes, which is tricky as many parameters are involved. This insight is needed to tailor the material combinations to meet the specifications required by the user.

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